

mineral aerosol deposition. XRD results indicate that primary minerals including pyroxene, plagioclase, and pseudobrookite are quickly weathered out of the soils, replaced with amorphous sesquioxides by the 20 ka and 150 ka sites. Crystalline sesquioxides and anatase are seen in the oldest soils. Dust-derived minerals including quartz are evident in all soils older than 20 ka. The profile of U with depth through the soil strongly correlates with the distribution of iron oxides in the profiles. Between 0.2% and 1.2% of the total U in our soils was extracted with ammonium acetate, indicating that very little U exists as exchangeable cations in any of these soils. A second extraction, employing citrate-dithionate and hydroxylamine hydrochloride, was performed to extract U associated with iron oxides. Average percent occurrences for U in the second extraction for each profile are, 9% at 2.1 ka, 48% at 20 ka, 36% at 150 ka, and 20% at 4100 ka, illustrating an increase with age to 20 ka and subsequent decline, paralleling the trend in amorphous iron oxide content, and suggesting that U becomes more permanently incorporated into the iron oxides as they recrystallize with age.

V22B-1228 1330h POSTER

Timing of Lithofacies Development in Rift Sediments of Lake Baikal (Siberia, Russia)

Tomasz Sapota¹ (+46-18-471 2572; tomasz.sapota@geo.uu.se)

Ala Aldahan¹ (+46-18-4713095; ala.aldahan@geo.uu.se)

Goran Possnert² (+46-18-4713059; goran.possnert@angstrom.uu.se)

¹Uppsala University, Department of Earth Sciences, Villav. 16, Uppsala 752 36, Sweden

²Uppsala University, Angstrom Laboratory, Lgerhydsdv. 1, Uppsala 751 21, Sweden

This work has been based on samples collected from, so far, the deepest borehole (core BDP-98, 600 m deep) penetrating sediment at the Academician Ridge (53 deg 4' N and 108 deg 2' E, water depth of 333 m) in Lake Baikal (BDP-Members, 2001). The Academician Ridge, structural and bathymetrical high between central and south Baikal basins with limited influence of turbidity flows, represents a suitable site for retrieval of paleoclimatic and tectonic records. The scope of the investigation includes a survey of the sedimentological, mineralogical and geochemical variability in the sediment section. Studied samples, initially aimed for Be-10 dating, have been chosen to represent different lithofacies and subjected to examination by various analytical methods including grain size analyses (laser based grain size analyzer), mineralogy (X-ray diffractometry and light and electron scanning microscopy), chemistry (ICP MS). The studied samples are dominated by silt-size particles with variable content of diatoms. The inorganic particles are composed of quartz, plagioclase feldspar, K-feldspar, clay minerals (micas, chlorites, and kaolinite), carbonates (calcite and siderite), Fe-minerals (oxides and sulfides) and Ti-minerals. We observe no specific variability in mineralogy with respect to the three major facies that spread from the deltaic one at the bottom of the section (dated at 8-7 Myr) through the hemipelagic (dated at 5.5-3 Myr) to the glacial (<3 Myr). The chemical data show a generally down core decrease in silica and increase in alumina and loss on ignition. The explanation for this likely to be a higher diatom content in the hemipelagic and Quaternary facies compared to the deltaic one. Apart from strong fluctuations in each facies, the general trends of trace elements are fairly constant down core. Samples enriched in vivianite (Fe₃(PO₄)₂ · 8H₂O), concretionary siderite (FeCO₃) and occasionally nests of framboidal pyrite (FeS) occur throughout the facies. There is apparent association of Fe, Mn and P in the sediments that is related to these minerals. This association is produced probably by rift-related pulses of hydrothermal activity that took place at the end of the major volcanic episodes in this region at about 8 Myr ago. The expected origin of siderite microconcretions is probably diagenetic alteration of organic material (e.g. fecal pellets) by Fe-rich hydrothermal fluids. These alterations will be a target of detailed diagenetic investigations in future.

References

BDP-Members, 2001. The new BDP-98 600-m drill core from Lake Baikal: a key late Cenozoic sedimentary section in continental Asia. Quaternary International, 80-81, p. 19-36.

V22B-1229 1330h POSTER

Monte Carlo Simulations of hydration of mono- and divalent cation exchanged (SWy-1 and SAz-1) montmorillonite

Sung-Ho Park¹ (510-643-3172; SungHo.Park@lbl.gov)

Garrison Sposito¹ (510-643-8297; GSposito@lbl.gov)

¹Lawrence Berkeley National Lab, Geochemistry Department, Earth Sciences Division, Mail Stop 90/1116, Berkeley, CA 94720

Monte Carlo simulations were carried out to study the hydration of montmorillonite. Two different type of montmorillonite (SWy-1 and SAz-1) were investigated with monovalent (Na⁺ and Li⁺) and divalent (Ca²⁺ and Mg²⁺) interlayer cations. The hydration of each system was systematically simulated from dehydrated state up to 10 layers of molecular water (over 53 water molecules per cation). The effect of interlayer cation type, interlayer cation charge, the type of clay mineral, and interlayer hydration on the structure and the properties of adsorbed water were analyzed. Interlayer water structure at varying water content was also monitored and compared with that of bulk water.

URL: <http://esd.lbl.gov/GEO/aqueous-geochem>

V22B-1230 1330h POSTER

Acquisition and Evaluation of Thermodynamic Data for Morenosite-Retgersite Equilibria at 0.1 MPa

I-Ming Chou¹ (703-648-6169; imchou@usgs.gov)

Robert R. Seal¹ (703-648-6290; rseal@usgs.gov)

¹U.S. Geological Survey, 954 National Center, Reston, VA 20192, United States

Metal-sulfate salts are common minerals found in mine drainage environments, and thermodynamic data for these salts are needed for constructing paragenetic models as well as formulating remediation strategies. Thermodynamic data for these salts are either not available or in poor agreement. However, recent development of the humidity-buffer technique (Chou et al., 2002, Amer. Mineral., 87, 108-114) provides an efficient and reliable method for obtaining and evaluating these data. These salts commonly occur in nature as solid solutions and can contain Fe, Cu, Mg, Zn, Al, Mn, Ni, Co, Cd, and other elements. To establish a useful thermodynamic database for the interpretation of natural assemblages, it is necessary to first study thermodynamic properties of end member salts (Chou et al., ibid. for Fe and Cu; Chou and Seal, 2001, Goldschmidt Conf., p. 3114.pdf for Zn, and Chou and Seal, 2001, GSA Abstr. With Progr., 33, p. A-403 for Mg). This study extends the database to the Ni end-member system; dissolved Ni has known toxicity to aquatic ecosystems in mine drainage settings.

Published estimates for the equilibrium relative humidity (RH) for the reaction: Morenosite (NiSO₄ · 7H₂O) = Retgersite (NiSO₄ · 6H₂O) + H₂O, at 25°C range from 67 to 96%. To evaluate these data, the humidity-buffer technique (Chou et al., 2002, ibid.) was used to determine equilibrium constants for this reaction between 5 and 22°C at 0.1 MPa. Reversals along five humidity-buffer curves yield ln K = 17.58 + 6303.35/T, where K is the equilibrium constant, and T is temperature in K. The derived standard Gibbs free energy of reaction is 8.84 kJ/mol, which agrees very well with the values of 8.90, 8.83, and 8.85 kJ/mol based on the vapor pressure measurements of Schumb (1923, J. Am. Chem. Soc., 45, 342-345), Bornell and Burridge (1935, Trans. Faraday Soc., 31, 473-478) and Stout et al. (1966, J. Chem. Phys., 44, 405-409), respectively. However, this value is considerably different from the values of 8.65 and 9.56 kJ/mol calculated from the data compiled by Wagman et al. (1982, J. Phys. Chem. Ref. Data, v. 11, Sup. No. 2) and DeKock (1982, Bur. Mines Inf. Cir., 9810), respectively. Many previous observations indicate that the temperature of the invariant point for the assemblage morenosite-retgersite-aqueous solution-vapor is near 31.2°C (Link, 1965, Solubilities, vol. 2). When extrapolated to this temperature, our data predict RH = 95.6% at this invariant point, which agrees reasonably well with RH = 92.0% predicted by Pitzer's model for solutions saturated with both morenosite and retgersite (Reardon, 1989, J. Phys. Chem., 93, p. 4630, and pers. comm.).

V22B-1231 1330h POSTER

The Role of Localized Reducing Zones in Cr(VI)aq Removal by the Hanford Sediments Under Hyperalkaline Conditions

Nikolla P. Qafoku¹ ((509) 375-4364; ntk.qafoku@pnl.gov)

Peter C. Lichtner² (lichtner@lanl.gov)

Calvin C. Ainsworth¹ (calvin.ainsworth@pnl.gov)

¹Pacific Northwest National Laboratory, MSIN: K3-61 902 Battelle Boulevard, Richland, WA 99352, United States

²Los Alamos National Laboratory, EES-6; MS D469 SM-30 Bikini Atoll Rd., Los Alamos, NM 87545, United States

High level waste fluids (HLWF) with high pH and ionic strength and rich in Cr(VI) have leaked from underground single shell storage tanks at the Hanford

Site, WA. A recent study of the sediments cored beneath the tanks indicated that Cr(VI) migrated faster than 137Cs but was retarded with respect to 99Tc. Our previous experimental work also showed that CrO₄-2 transport was retarded under extreme alkaline conditions. Decreased mobility of CrO₄-2 was the result of base catalyzed mineral dissolution, subsequent release of Fe(II) from Fe(III)-bearing soil minerals (biotite and chlorite), and, ultimately, Cr(VI)aq reduction by Fe(II)aq to less mobile Cr(III).

If CrO₄-2 attenuation occurs via reduction, the presence of localized reducing conditions is required in the inherently oxidized environment of the Hanford vadose zone. These O₂-depleted zones may be created when Fe(II) is released during dissolution. Our objective, therefore, was to investigate the role of the localized reducing zones created during mineral dissolution, in the attenuation of CrO₄-2.

Batch experiments with Hanford sediments and simulated HLWF were conducted at 323 K in the presence or absence of oxygen. Sediments were contacted with 0.192 M Cr(VI), 1M NaNO₃ and varying concentrations of NaOH and Al solutions, and the changes in the soil solution composition as a function of time were followed.

Results showed that while the presence or absence of O₂ had no apparent effect on the extent of dissolution (similar trends of the Si and Fe release were observed in the O₂-free and O₂-rich experiments), CrO₄-2 fate was closely related to the presence of O₂ in the system. By the end of experiments (42 days), the initial CrO₄-2 was totally removed from the aqueous phase in the experiment where base-induced dissolution occurred under O₂-free conditions. In this experiment, the rate of CrO₄-2 removal was closely related to the extent of sediment dissolution. In contrast to the O₂-free experiment, only a limited amount of CrO₄-2 was removed from the aqueous phase in the treatments of the experiment where dissolution occurred in the presence of O₂. Appreciable CrO₄-2 removal was only observed in the Al-free, 4 M NaOH treatment of the O₂-rich experiment. The decreasing trend of CrO₄-2 concentration with time observed in this treatment was very similar to the trend observed in its O₂-free counterpart. Dissolution of the soil minerals probably mobilized substantial quantities of Fe(II) in this treatment. It is likely that a portion of the Fe(II) released into the soil solution consumed the O₂ creating localized zones with predominantly anoxic conditions and excess Fe(II)aq where Cr(VI) reduction may have occurred.

In order to better understand quantitatively the behavior of Cr(VI) in the Hanford sediments, a modeling strategy was pursued to first model the relatively simpler batch systems without Cr, followed by batch systems in the presence of Cr. The results from these experiments were modeled using the reaction path option of the computer code FLOTTRAN. Because of the high ionic strength of the fluids, the Pitzer model was used to calculate activity coefficient corrections. Preliminary results suggest a reasonably good fit to the experimental data can be obtained for these batch experiments. This work will provide the foundation for modeling more complex column experiments and field-scale contaminant plumes involving Cr(VI).

V22B-1232 1330h POSTER

Chromium Geochemistry in Serpentinized Ultramafic Rocks and Serpentine Soils from the Franciscan Formation of California

Christopher J. Oze¹ (oze@pangea.stanford.edu)

Scott E. Fendorf¹ (fendorf@pangea.stanford.edu)

Dennis K. Bird¹ (bird@pangea.stanford.edu)

Robert G. Coleman¹ (coleman@pangea.stanford.edu)

¹Stanford University, Department of Geological and Environmental Sciences, Stanford, CA 94305-2115

Weathering of ultramafic rocks and their metamorphic equivalents (serpentinites) in the Franciscan Formation of California produces serpentine soils containing high concentrations of chromium as well as potentially toxic elements such as nickel, cobalt, and manganese. Chromium concentrations in serpentine soils from Jasper Ridge Biological Preserve in the Central Coast Range are as high as 15,000 mg/kg, an order of magnitude greater than the serpentinite protolith (approximately 1600 mg/kg). Chromium-containing minerals within the bedrock include chlorite (~ 0.4Cr₂O₃ Wt. %), enstatite (~ 0.6Cr₂O₃ Wt. %), augite (~ 1.0Cr₂O₃ Wt. %), chromite (~ 15.8Cr₂O₃ Wt. %), magnetite (12.0-15.0 Cr₂O₃ Wt. %), and an ultra fine-grained mixture of chromite and a silicate phase containing ~ 19.4Cr₂O₃ Wt. %. Chromium concentrations with respect to depth in the soil profiles are highly variable demonstrating both maximums and minimums. The enrichment and variability of chromium in the soils is directly related to the modal abundance and weathering of chromite, chromium-magnetite, and the chromite-silicate mixture. Chemical analyses and elemental maps demonstrate that chromium-oxides in